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MICROSTRUCTURAL ASPECTS OF THE STRENGTH AND HARDNESS OF CEMENTED TUNGSTEN CARBIDE

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1. Tungsten carbide, cemented
2. Materials research
3. Tool materials

II

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The balance of hardness and strength in sintered tungsten carbide-cobalt alloys is obtained by adjusting cobalt content and particle size of WC. The variations of hardness and strength with composition and particle size are discussed in this paper in terms of the mechanical interaction of the hard and ductile phases. The observed increase of hardness and yield strength with decreasing cobalt content and decreasing particle size is attributed to the plastic constraint of the cobalt layers in contact with the tungsten carbide. The plastic constraint also causes a transition between ductile and brittle modes of fracture, which, in turn, accounts for the observed maximum of fracture strength at small values of the carbide spacing. The theories of fracture pertaining to compositions of commercial alloys are based on the Griffith-Orowan equation, the parameters of which have been empirically related to the microstructure. Further progress in the design of WC-Co alloys can be achieved by control of the microstructure and the potential improvement of mechanical properties obtainable by the control of a number of variables is briefly mentioned.

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[redacted]

The two important constituents of metallic tool alloys are the carbides (Fe_3C, M_6C, WC, etc.) and the metals of the iron group (Fe, Ni, Co). Neither of the constituents is by itself a satisfactory tool material, since the carbides are brittle and the metals are soft. However, together they combine into alloys which are both hard and tough. In the context of tool materials, hardness is a measure of the resistance to penetration and abrasion, and toughness is the ability to absorb energy by deformation without cracking.

The early development (before 1914) of tool materials was based on the metallurgy of steels and consisted mainly of increasing the amount and hardness of the carbide constituent; this led in turn to high-carbon tool steels, alloy tool steels and cast cobalt-base alloys. Further progress was limited by the difficulty of processing (i.e. cold and hot working and casting) alloys with increasingly higher hardness, brittleness and melting temperatures. When, after the first World War, attention turned to tungsten carbide, it was found that the standard processing methods were totally impractical and that powder metallurgy techniques were required for its commercial exploitation. The critical step in the development was probably the use of cobalt as the binder metal by K. Schröter (1927). The addition of cobalt to tungsten carbide not only allowed the sintering of dense compacts at reasonable temperatures, but also resulted in materials with adequate toughness at very high hardness levels.

The dual requirement of hardness <u>and</u> toughness is still central today to the design of modern tool materials. Whereas the problem with steels was that of increasing the hardness of basically tough metals, the

development of cemented carbides required the incorporation of a certain degree of toughness into hard but inherently brittle compounds. Hardness in a given alloy is contributed mainly by the carbide and toughness mainly by the metal. It is now realized that the two constituents exert highly beneficial effects upon each other, resulting, for instance, in strengths appreciably greater than the weighted average of the strengths of both in their unassociated conditions. The present article will attempt to discuss the strength and hardness of sintered tungsten carbide-cobalt tool materials on the basis of the mechanical interaction of the constituents in the microstructure. For more extensive surveys of cutting tool materials in general and of the strength theories of cemented carbides in particular, the reader is referred to the recent reviews by Trent[1] and Kreimer[2], respectively.

Evaluation of properties and properties of constituents.

The hardness of cemented carbides is usually determined by the Rockwell or Vickers hardness tests. The resistance to indentation, as measured by hardness tests, is related to the yield or flow stress.

Toughness and strength have different meanings although they are often used interchangeably with reference to cemented carbides. Strength is generally used to mean the fracture strength in tension or bending. Toughness is regarded as a measure of the energy absorbed before fracture; it may be evaluated experimentally from the area under the stress-strain curve in tension or from the work required to create cracks at hardness impressions. In practice, however, the transverse bend test has been widely used (by the author among others) to evaluate both strength and toughness of cemented carbides. For very brittle materials, the use of the transverse

rupture strength based on the elastic modulus of rupture is justified, but its application without correction to materials with considerable plasticity is of doubtful validity[2,3]. The maximum stress under conditions of perfect plasticity is only two-thirds of the elastic beam value at the same load. In defense of its widespread use, it ought to be stated that the transverse rupture test is relatively simple, the procedure is standardized, many results are available in the literature and, in trend, the results are similar to that of the tensile test. For lack of better data, much of the following discussion is based on the transverse rupture strength.

Tungsten carbide crystallizes in the hexagonal system. The equilibrium shape of WC crystals in the WC-Co alloy is that of triangular prisms, but the crystallites are not always well developed in sintered compacts. The microhardness of the crystals is reported as 2400-2500 kg/mm^2 [4]. The Vickers hardness of WC in the form of dense sintered compacts is 1600-1700 kg/mm^2 [2,4], and the transverse rupture strength is of the order of 100,000 psi.

Cobalt is present in the alloy as a solid solution containing from 2 to 10 weight % of tungsten, depending on carbon content and processing conditions[5]. The microhardness of the cementing phase in dilute WC-Co alloys (15-20 weight % WC) has been measured as 370-430 kg/mm^2 by Chaporava et al., as cited in reference 2. The tensile fracture strength of a sintered alloy of cobalt with 10 volume % of WC is 102,000 psi and probably approximates that of the cementing phase in bulk[6]. It should be noted that, in addition to structural and solutional effects, the properties of the binder are affected by the partial inhibition of the FCC/HCP phase transformation in thin films, on cooling.

Observed deformation behavior of WC-Co alloys.

Let us now consider the strength and hardness of the cemented carbide, i.e. of the mixture of WC with the cementing phase. After sintering the alloy consists of an aggregate of WC particles, the interstices of which are filled by the cementing phase. The latter will for simplicity be referred to as "cobalt" in the remainder of the article, although it is actually a solid solution.

The combination of strength and hardness requred for specific grades is obtained industrially by adjusting the composition, i.e. the cobalt content, and the particle size of WC. The effect of cobalt content on strength and hardness is shown in figure 1 with constant particle size ($\sim$ 2 μm). Yield stress and hardness decrease monotonically with increasing cobalt content, but tensile and bend strengths reach maximum values at intermediate compositions. Increasing particle size of WC affects the strength and hardness in a manner similar to that of composition, as indicated by the data of figure 2.

The low cobalt compositions (to the left of the strength maxima of figure 1) are generally regarded as brittle because they have little ductility before fracture, although there is a small amount of permanent deformation. The fracture path, as observed microscopically, is generally found at the interfaces of the WC particles if these are small ($\sim$ 2-3 μm), but larger particles are traversed by the fracture[7,8]. In alloys with cobalt contents to the right of the strength maxima of figure 1, the fracture takes place after considerable plastic flow and has been observed to initiate in the carbide particles in several alloys with large WC particles ($\sim$ 5μm)[6].

Commercial grades of WC-Co have compositions between 5 and 25 weight % cobalt (corresponding to 8.5 to 37.2 volume % cobalt) and range in average WC particle size from 4 μm to less than 1 μm. These grades lie generally to the left of the strength maxima of figures 1 and 2, i.e. in a range where the hardness and strength vary oppositely with changes of either composition or particle size. On the right side of the strength maxima, both properties increase with decreasing cobalt content or smaller particle size of WC, but unfortunately this rather appealing combination is not allowed in the present tool materials because the overriding requirement of adequate hardness limits these to the compositions and particle sizes indicated above.

Interpretation of mechanical behavior.

a) Flow stress and hardness

The deformation behavior of WC-Co alloys will now be related to the mechanical interaction of the constituents. It will be shown that the strength of the composite alloys depends primarily on the ability of the cobalt to deform plastically and that the embrittlement by low cobalt contents and small particle sizes is caused by internal stress conditions which suppress plastic flow.

The plastic flow of the layers of cobalt in the alloy is inhibited by the presence of the rigid WC. The local stress condition in a cobalt film is similar to that in a thin soldered or brazed joint in steel where the ductile joining metal is prevented from yielding at its bulk yield strength by the restraint of the elastically loaded steel. The recent works of Drucker[3] and Butler[9] examine the constraining effect of WC upon the cobalt by applying continuum mechanics on the microscale. They calculate a plastic

constraint factor for WC-Co aggregates of various compositions on the basis of a planar model of rigid hexagons separated by layers of perfectly plastic material, the hexagons representing the WC and the surrounding layers representing the cobalt. The constraint factor is defined as the ratio of the plastic limit stress required for fully plastic behavior of the ductile matrix in the aggregate to the yield stress of the matrix material. In the model the constraint factor is proportional to the ratio of layer thickness to hexagon side length, and in the cemented carbide it is determined by the thickness of the cobalt layers and the WC particle size. Drucker calculates the following values of the constraint factor (C.F.) and yield stress (Y.S.) in WC-Co as function of volume fraction of cobalt:

f_{Co}	0.10	0.19	0.25	0.31	0.37	0.50	0.70
C.F.	5.92	3.21	2.50	2.07	1.79	1.46	1.05
Y.S. ($\times 10^3$ psi)	240	130	100	83	72	58	42

The yield stress here is the 0.5% offset yield strength, based arbitrarily on a value of 40,000 psi for the yield strength of cobalt.

A high constraint factor means that the average stress on the composite must be a large multiple of the yield stress of the dultile constituent for widespread plastic deformation to occur[9]. Hardness, like flow stress, is expected to increase with the constraint factor up to a composition at which the direct contribution of the carbide becomes dominant or cracking occurs, at which point other factors would be determining.

Admittedly, the continuum treatment is based on a highly idealized and simplified model; it has, however, the advantage that the postulated mechanism of strengthening can be checked on models. Comparison of the

calculated yield strength with the measured proof stress of figure 1 shows fair agreement of strength ratios in the range from 20 to 50% Co, although the level of strength is underestimated. Part of the discrepancy may simply be due to the wrong value chosen for the yield strength of cobalt, but part may also be attributed to the size effect for the yield strength of cobalt in layers so thin (∿ 0.1 μm) that bulk properties can no longer be used as reference values. According to Drucker[3] this size effect becomes important when the dimensions of the cobalt layers are so small that the number of dislocations in each layer becomes a relevant variable. Continuum theory and dislocation theory overlap at this level of structure.

The microscopic treatments of flow strength which have been proposed (summarized in reference 2, also reference 10) are generally based on dispersion hardening theories. It has not yet been shown directly by observation that the specific dislocation mechanisms of dispersion hardening actually take place in the cemented carbides; these theories also involve either correction terms or constants, the numerical values of which have not yet been confirmed by theory or independent measurements. While the various approaches agree that the flow stress is determined by some measure of the thickness of the cobalt layers, it is clear that more work is required in order to establish unequivocally and quantitatively the relation between flow stress and structural parameters.

b) <u>Fracture strength</u>

The fracture strength is best discussed by referring to figure 3, which presents the transverse rupture strength as function of the nominal mean free path, i.e. the average distance in the cobalt between carbide

particles:

$$p = \ell \frac{f}{1-f} \qquad (1)$$

where p is the mean free path, ℓ is the mean linear intercept particle size of WC and f is the volume fraction of cobalt. This representation has the advantage of combining both composition and particle size into one parameter. The nominal mean free path, as used by Gurland and Bardzil[7], is based on an idealized structure in which all particles of WC are regarded as non-contiguous. In a similar representation, Exner and Fischmeister[11] introduce a "true" mean free path:

$$p_p = \frac{\ell}{1-C} \frac{f}{1-f} \qquad (2)$$

which takes into account the contiguity C, a measure of the degree of contact between WC particles.

As indicated in figure 3, the curves show a transition between brittle and ductile behavior. To the right of the strength maximum, the "ductile" side of the diagram, failure takes place between the limit load of the composite based upon the yield strength of the cobalt and the limit load corresponding to the ultimate strength of the cobalt[3]. The fracture strength of the composite depends on the critical stress for crack initiation in the carbide particles or elsewhere in the microstructure. The fracture mechanism is ductile in the sense that failure occurs by an accumulation of damage in the structure under increasing loads--for instance, by cracking of carbide particles (as observed by Nishimatsu and Gurland[6])--until the aggregate fails when a critical number of particles are broken and the remaining material can no longer support the load.

The fracture mechanism to the left of the strength curve is brittle in the sense that failure occurs by catastrophic propagation of fracture from a critical flaw. It may be seen from figure 1 that the fracture strength in tension lies below the proof stress or limit load in yielding. The constraint factor is so high that plastic deformation does not take place to any appreciable extent, with the consequence that local stress concentrations are not relaxed by plastic flow and instead contribute to fracture initiation and propagation. It may be argued that an increase of the mean free path raises the fracture strength because it decreases the constraint factor and the peak stresses in the aggregate.

In brittle materials in general the fracture strength is determined by the critical conditions for crack propagation and the Griffith-Orowan criterion provides a quantitative correlation between fracture strength and microstructural parameters of brittle alloys:

$$\sigma = k \left(\frac{Ep}{\ell_C}\right)^{1/2} \tag{3}$$

where σ is a critical fracture stress, k is a constant, E is the modulus of elasticity, p is the total work of fracture and ℓ_C is the length of the initiating crack or other discontinuity. The application of the Griffith or Griffith-Orowan criteria to cemented carbides is most extensively developed by Kreimer and his co-workers (summarized in reference 2), and is also the basis of fracture theories proposed by Exner and Fischmeister[11], Gurland[12], and Nabarro and Luyckx[13]. In order to justify the relevance of this fracture criterion to cemented carbides, the separate influence of the physical parameters E, p and ℓ_C will now be examined.

The elastic modulus E enters into equation (3) through its con-

tribution to the strain energy and it appears reasonable that this represents the modulus of the alloy and is so used by Kreimer. The major contribution to the modulus of an alloy of tool grade composition, i.e. rich in WC, is the value of the modulus of the carbide constituent; if all other terms are constant, the fracture strength should be proportional to that modulus. The results of one study[14] support this relation to some extent, as shown in table 1. The table compares the strengths of various carbide-cobalt alloys at two different cobalt contents and shows that the strengths increase in the same order as the values of the moduli of the carbides.

The major part of the work of fracture, p, is undoubtedly contributed by the work of plastic deformation of the cobalt in the crack path. Figure 4 reproduces the data of Kreimer et al.[2] as a plot of fracture strength (σ) against the product of cobalt content in weight percent (C) and the elastic modulus (E). The observed linear relation permits Kreimer et al. to propose the following equation for the strength of brittle cemented carbides:

$$\sigma^2 = AEC + K \tag{4}$$

where A and K are constants. The equation is derived from equation (3) by postulating that the plastic work of fracture is proportional to the area fraction of the fracture surface in the cobalt phase, which in turn is proportional to the weight fraction (more accurately, volume fraction) of cobalt in the alloys. It is interesting to note that the slope constant A is independent of particle size and that the particle size appears only in the intercept value K. According to Kreimer[2], the characteristics of the constants mean that the plastic work in the cobalt is not affected by the particle size of WC at a given composition and that the value of K is

related to the contribution to the fracture stress of the tungsten carbide itself. Indeed, it is observed that K increases with particle size, as would be expected since the fracture path preferentially traverses the larger WC particles.

Little is known about the physical significance of the parameter ℓ_C in equation (3), which, in Griffith's model, is the critical length of the crack nucleus. In Kreimer's derivation of equation (4), ℓ_C is contained in the constant A together with the work of fracture per unit of cobalt content. It is experimentally difficult to separate the two variables and it is often necessary to assume the magnitude of one of them. Gurland[12], for instance, plotted the maximum strength of four compositions (63, 69, 75 and 81 volume % WC) from the data of figure 3 against the reciprocal of the square root of the particle diameter of WC. As shown in figure 5, the relation is approximately linear, within the limited range of the data. From the Griffith-Orowan equation and the slope of the line of figure 5, a value of 9000 ergs per cm^2 is calculated for the work of fracture. Whether or not this is a reasonable value depends on the validity of the assumption that ℓ_C is proportional to the particle size of WC. In Gurland's work, this assumption was based on the observed cracking of large WC particles in these alloys[6] and the postulate that the maximum strength is attained at the transition from the "ductile" mode of fracture to cleavage. As in most brittle fracture theories, the value of ℓ_C cannot be verified unless the work of fracture is independently established, and vice versa.

Here, again, it must be concluded that further work in relating the strength to structural parameters is required before the Griffith-Orowan criterion can be applied quantitatively to cemented carbides. In the

meantime, the equation of Kreimer and co-workers (eq. 4) serves as a useful approximation describing the observed behavior.

Discussion of the control of microstructure.

The preceding discussion suggests certain guidelines for alloy improvement. The argument might be based on figure 6, a schematic summary of figures 1-3, and on the desire to improve on the properties of the alloys on the solid line AB. Extrapolating line A to the right (A') leads into a region of increasing strength but decreasing hardness and therefore does not appear profitable. However, extrapolation of curve B to the left (B') points towards alloys of both higher strength and greater hardness, a very desirable direction. This would imply, of course, the ability to shift the transition between fracture modes towards the left by control of the microstructure. As a matter of speculation, the extrapolation to the limit could reach the hardness of fine grained WC (> 2000 kg/mm^2 HV) at strength levels of upwards of 700,000 psi[15]. While this ideal limit might not soon be attained, the more immediate alloy development will perhaps take place with microstructures and properties located in the shaded region between line A and the extrapolated line B'. Examining, for instance, the data of figure 3 one notices that the strength increases on the brittle side of the graph and at constant value of the mean free path, with greater cobalt contents, i.e. smaller WC particles sizes. One of the main requirements is the achievement of a highly uniform distribution of the cobalt in the microstructure, which, in turn, requires reducing the contiguity of WC. Butler[9] points out that a reduction of contiguity at constant mean free

path entails either an increase of the cobalt content or a decrease of the WC particle size (see equation 2). According to continuum analysis, either or both of these changes tend to raise the fracture strength at a fixed value of the mean free path.

Among the problems encountered in attempting to evaluate theories and experimental results is the general neglect in the scientific literature of variables other than cobalt content and average particle size of WC. Among these are carbon content, impurity content, porosity, particle size distribution and thermal history. A review of parameters influencing the mechanical properties may be found elsewhere[16].

As one example of the importance of one of these parameters, figure 7 shows the marked effect on strength of variation of carbon content, even within limits generally considered safe. The data is from the work of Suzuki[5] as plotted by Butler[9] and the shape of the curves is consistent with the plastic constraint and Griffith-Orowan theories. Another example of the large effect of small compositional changes is provided by the work of Montgomery[17] on the effect of various surface coatings on the wear behavior of cemented carbides. He found that thin coatings ($\sim$ 100 μinch) of gold, tin, silver, manganese, freshly deposited titanium, lead, tin, bronze and solder on a cemented carbide surface allow a WC-Co slide to operate at least 10,000 cycles at conditions which cause surface fatigue of the same slides on uncoated carbide in only 100 cycles. The author suggests that diffusion of the coating material may diminish the tensile stresses normally present in the cobalt and thereby increase the fatigue strength.

Finally, reference should be made to the interesting study of the polar anisotropy of WC by French and Thomas[18]. Following up the recent

discovery of slip in WC crystals, these authors found that WC crystals have different properties along different senses of the crystallographic direction $[10\bar{1}0]$. Parallel prism faces $(10\bar{1}0)$ and $(\bar{1}010)$ differ in etching characteristics, wettability by polar liquids and microhardness. It is possible that preferred orientation of the crystallites of WC in the alloys might produce an anisotropy of properties of the aggregate which has not yet been studied or exploited.

It is obvious from the preceding discussion that not enough is known about the design of cemented carbide tool materials in spite of an appreciable increase in knowledge about their properties during recent years. The industry shows signs of entering an era of renewed activity in grade development and materials design and it is to be hoped that some of the new ideas will come from the kind of materials research discussed in this survey.

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TABLE 1

Comparison of Strength of Cemented Carbides[14]

Carbide	Elastic Modulus, x 10^6 psi	Transverse Rupture Strength, x 10^3 psi	
		10 vol. % Co	37 vol. % Co
WC	102	241	346
TaC	57	163	269
TiC	51	162	254
NbC	49	132	205
VC	37	83	183
ZrC	20	37	113

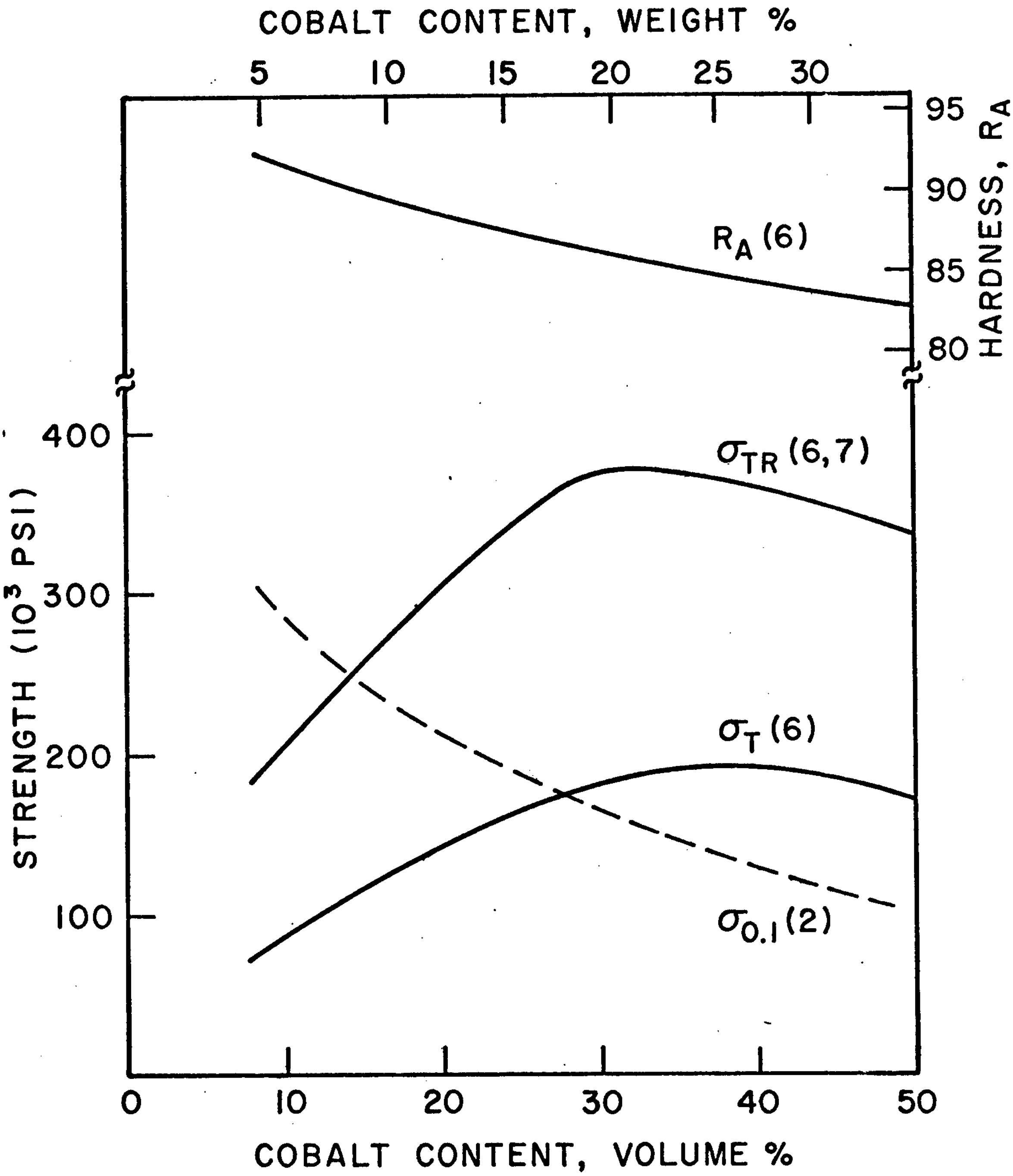

FIG. 1 TRANSVERSE RUPTURE STRENGTH (σ_{TR}), FRACTURE STRENGTH IN TENSION (σ_T), PROOF STRESS AT 0.1% STRAIN IN COMPRESSION ($\sigma_{0.1}$) AND HARDNESS (R_A) AS FUNCTION OF COBALT CONTENT. (WC PARTICLE SIZE APPROXIMATELY 2μm)

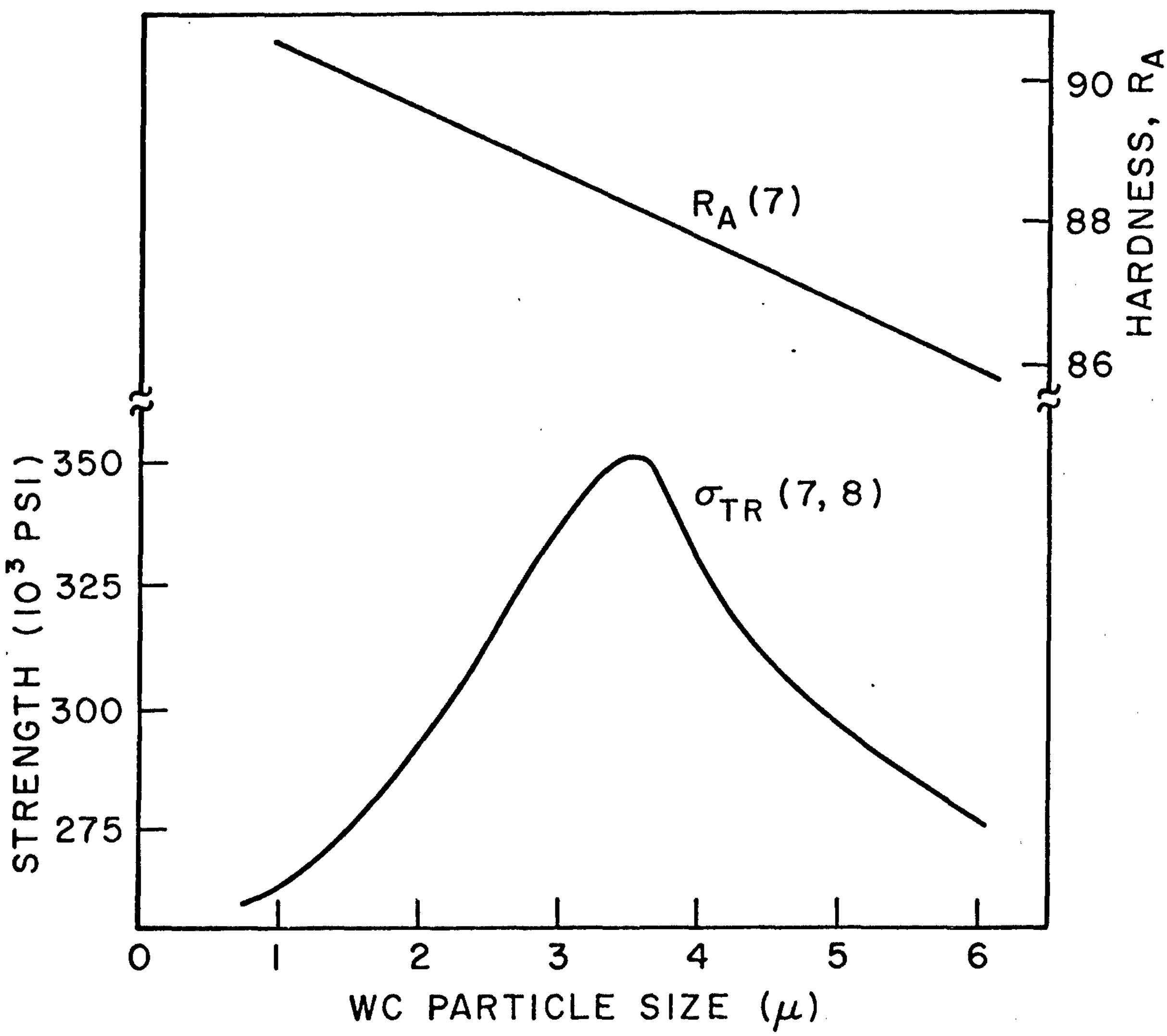

FIG. 2 TRANSVERSE RUPTURE STRENGTH AND HARDNESS AS FUNCTION OF AVERAGE PARTICLE SIZE OF WC. COMPOSITION: 20 VOL. % Co. (16)

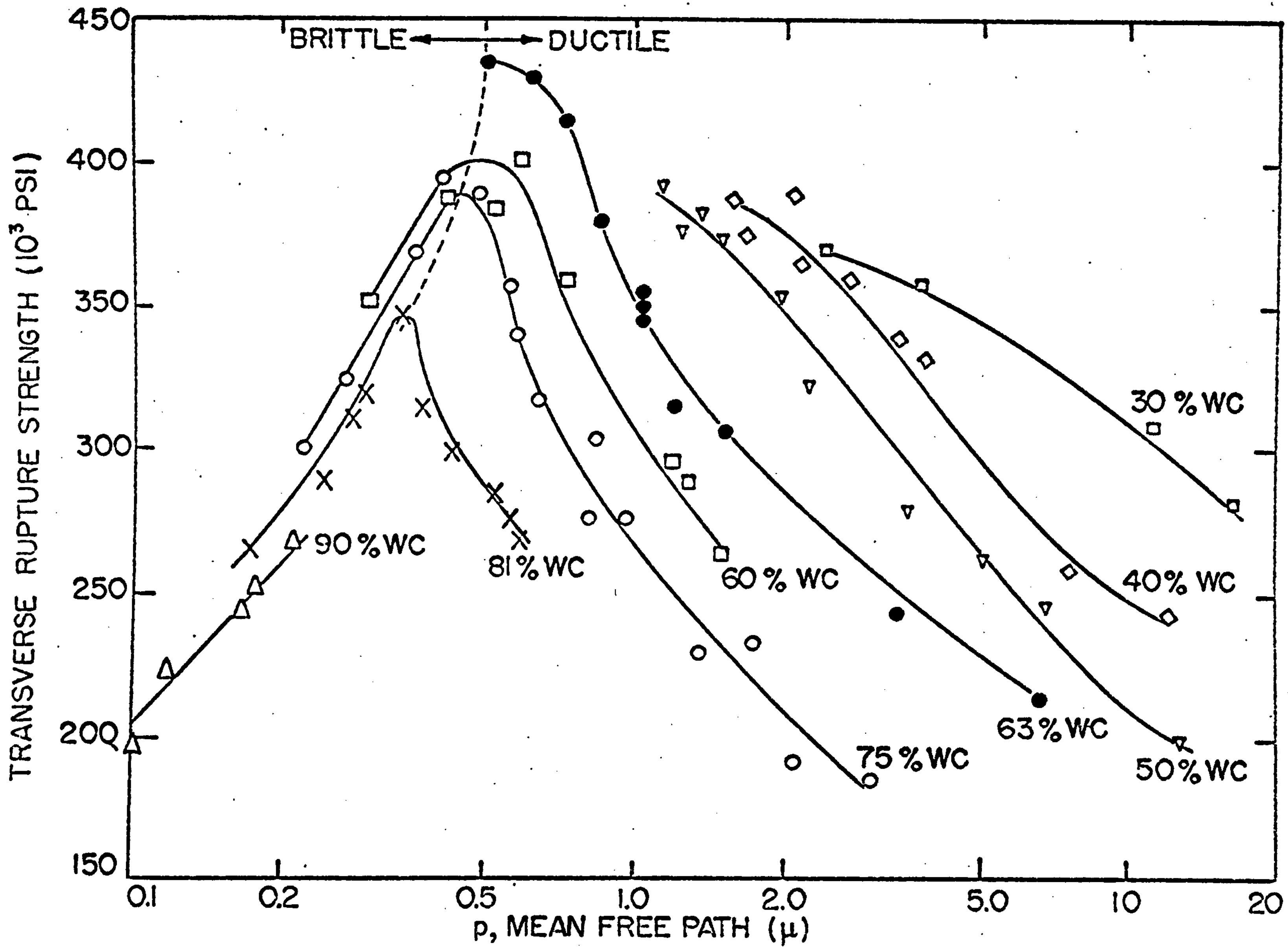

FIG. 3 TRANSVERSE RUPTURE STRENGTH VERSUS MEAN FREE PATH (12).

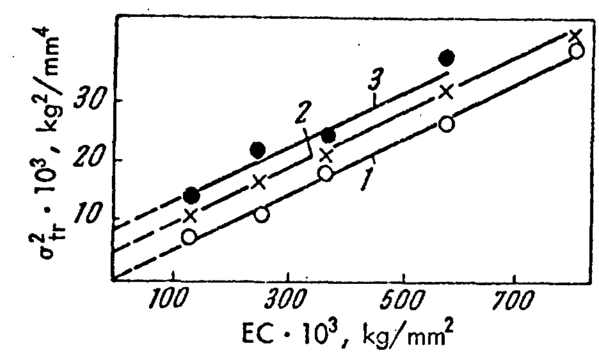

FIG. 4 PLOT OF SQUARE OF TRANSVERSE RUPTURE STRENGTH (σ_{TR}) VERSUS PRODUCT OF MODULUS OF ELASTICITY (E) AND COBALT CONTENT (C). MEAN CARBIDE PARTICLE SIZE 1) 1.64 μ, 2) 3.3 μ, 3) 4.95 μ. (AFTER REF. 2, FIG. 74)

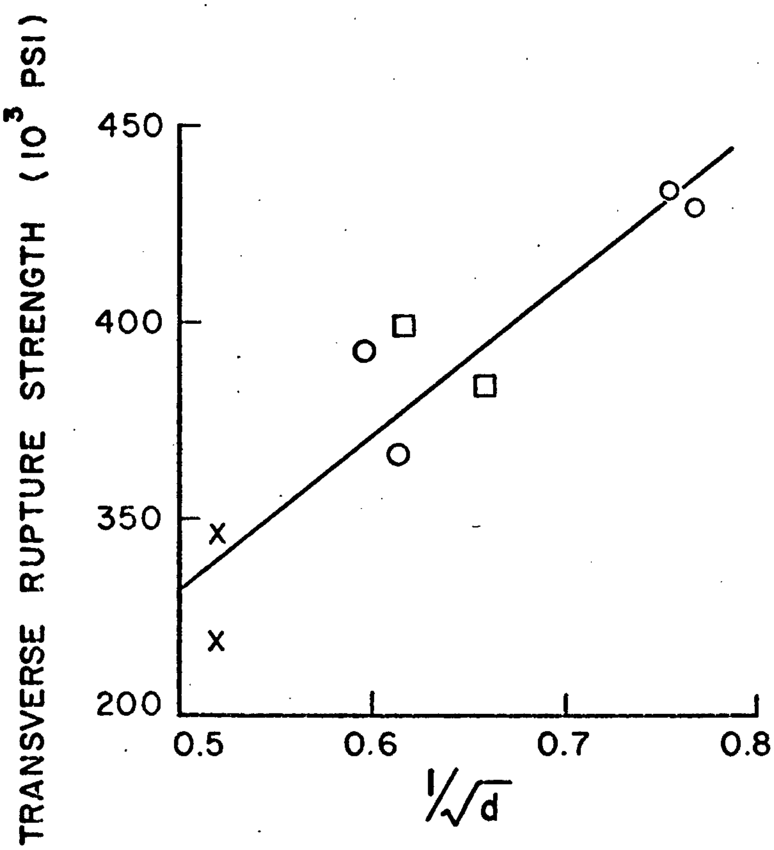

FIG. 5 TRANSITION STRENGTH

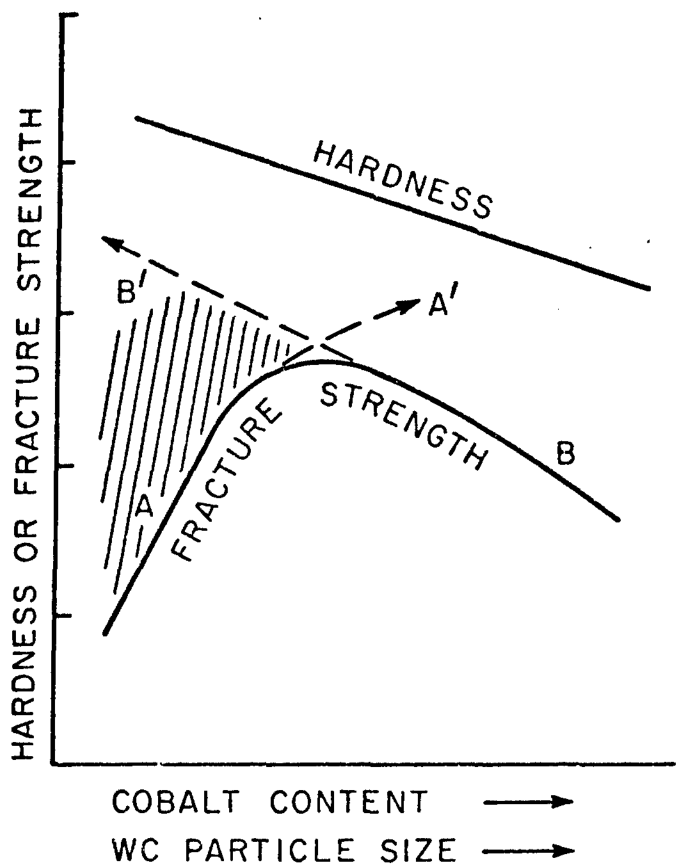

FIG. 6 SCHEMATIC REPRESENTATION OF VARIATION OF STRENGTH AND HARDNESS WITH COMPOSITION AND PARTICLE SIZE.

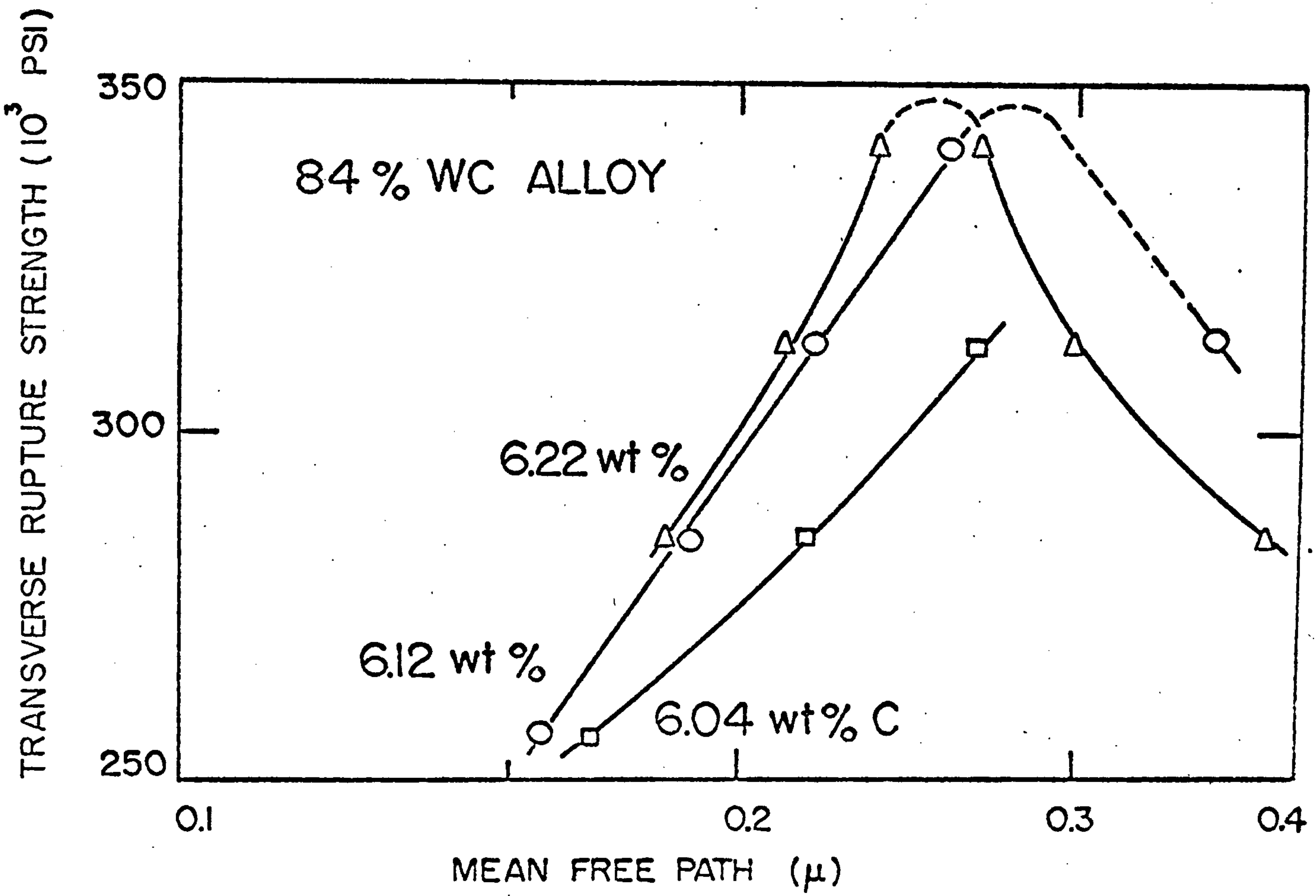

FIG. 7 STRENGTH AS FUNCTION OF CARBON CONTENT AND MEAN FREE PATH (AFTER 5 AND 9).